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CHROMATOGRAPHIC AND RELATED REACTORS(U) WISCONSIN
UNIV-MADISON DEPT OF CHEMICAL ENGINEERING S H LANGER
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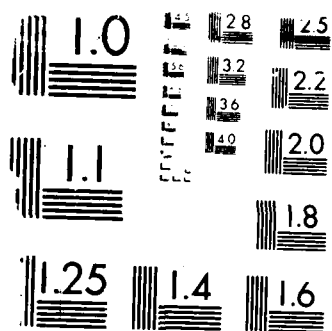
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Several variations of gas and liquid column chromatographic reactors were investigated. In connection with this, new information on the kinetics and course of the base catalyzed esterification reaction of tetrachloroterephthaloyl chloride and its derivatives was obtained with Carbon-13 Nuclear Magnetic Resonance. The operation and conversion in a reverse phase liquid chromatographic reactor could be analyzed on a quantitative basis when consideration was given to the associative interaction between the stationary phase and elements of the mobile phase. Furthermore, the composition and models for the stationary phase could be examined on the basis of the kinetics of reaction of the tetrachloroterephthaloyl derivatives. A related procedure for determining the phase ratio was developed. Mass transfer limitations for chromatographic reactions were also analyzed. Incorporation of a void column between two packed liquid chromatographic columns made it possible to decouple esterification rate constants for both the mobile and stationary phase. The stopped flow liquid chromatographic reactor was found to be viable for conver-			
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sions and operation but not amenable to quantitative analysis because of ionic strength effects with our systems. Operation of a version of the stopped flow gas chromatographic reactor was successful and applications to studies of catalytic reactions were demonstrated. The rate of the CO methanation reaction even could be measured at room temperature on supported nickel, ruthenium and cobalt catalysts. Mass transport effects were studied in a stopped flow gas chromatographic reactor and it was demonstrated that the stopped flow reactor could be utilized with Temperature Programmed Reaction to obtain special information about effects of surface heterogeneity in the methanation reaction. Studies of an efficient multicolumn assembly for measuring kinetics, illustrated for vapor phase dissociation reactions of cyclopentadiene dimers, were also completed.

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CHROMATOGRAPHIC AND RELATED REACTORS

FINAL REPORT

STANLEY H. LANGER

JANUARY 7, 1988

U.S. ARMY RESEARCH OFFICE

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CHROMATOGRAPHIC AND RELATED REACTORS

This program was directed toward expanding use of chromatographic reactors and investigating how their applications might be broadened. Because of their limited development, liquid chromatographic reactors received special emphasis. Thus a number of variations of gas and liquid column arrangements utilized as chromatographic reactors were investigated and their operations analyzed. In association with this, kinetics for several reactions and special separations were also studied. These are described below in separate sections.

LIQUID CHROMATOGRAPHIC REACTORS

In the course of this work we completed an elucidation of the mechanism of the methanolic solvolysis of our model compound, tetrachloroterephthaloyl chloride (TCTPCl₂), in both the presence and absence of organic basic catalysts such as pyridine and 4-methylpicoline. It was demonstrated that the chromatographic reactor gave special information about the course of reaction which could be clarified with NMR. With a knowledge of the base catalyzed solvolysis rate in a methanolic mobile phase, it was possible to obtain data which could be interpreted to estimate the amount of methanol associated with bound hydrocarbon ligands in the stationary phase, a type of information that is difficult to obtain by other means. Models for the stationary phase structure were also examined with these data. The procedure stems from a measure of k_{apparent} (the apparent rate constant) for the reaction in the liquid chromatographic column. From this and retention volume data it was possible to determine conversion in both the stationary and mobile phase. However, this determination was based on "ideal" chromatographic behavior. Such behavior turns out to be more limited in liquid chromatography than with gas chromatography because of mass transport processes. This is because these are slower (by a factor of 10^3) in liquid chromatography than with gas chromatography. Because the extension of chromatographic reaction rate measurements to reactions occurring in liquid chromatographic columns would expand the applications of these systems, the effects of mass transport processes were examined.

Commonly employed chemically bonded ODS columns were studied with the TCTPCl₂ reactant under pseudo-first order reaction conditions. The physical rate processes considered were longitudinal diffusion, micropore diffusion and sorption-desorption kinetics across the mobile phase-stationary phase boundary. Under the standard conditions of modern chromatography there did not seem to be a significant effect on first order rate constants of 10^{-4} s measured here compared to batch reaction data at 35°C. The conclusions and models of this study were summarized in a published manuscript.

Incorporation of a void column between two packed liquid chromatographic columns was shown to make it possible to decouple esterification rate constants for the mobile phase from that of the stationary phase. The value of this was discussed and illustrated. It was further shown that on-column rate constants in a bonded stationary phase could be used to determine the "phase ratio" for the operating column as well as the catalyst distribution coefficient. The results obtained from the operational approach potentially can be expanded to other systems.

During the final part of this investigation, the stopped flow liquid chromatographic reactor was studied and found to be operational and viable for

conversions of TCTPCl_2 . However, the kinetics were resistant to quantitative analysis because of ionic strength effects in the systems that we were investigating. Changing ionic strength not only affects the rate of reaction in the mobile phase but it also affects the association of mobile phase with the bonded stationary phase. Thus, the composition of the stationary phase with associated alcohol changes also affecting the rate of esterification in that phase.

GAS CHROMATOGRAPHIC REACTORS

Operation of a sensitive version of the stopped flow gas chromatographic reactor was successful and applications to studies of catalytic reactions were demonstrated. The rate of the CO methanation reaction was studied in the range of 300 to 500 K. It was shown that the rate even could be measured at room temperature on alumina-supported nickel, ruthenium and cobalt catalysts. Not only were mass transport effects studied in a stopped flow gas chromatographic reactor but it was demonstrated that the stopped flow reactor could be utilized with Temperature Programmed Reaction to obtain special information about surface heterogeneity in the methanation reaction. Advantages of stopped flow over steady state reactor operation were demonstrated. The analysis of the kinetics of the methanation reaction is complicated by what appears to be a bimodal distribution of reaction sites. In steady state reactors it is probably the most active sites which are responsible for conversion.

Analysis of the operation of an efficient multicolumn chromatographic reactor assembly for studying the kinetics of vapor phase reactions was also completed. The kinetics of the dissociation reactions of dimers of cyclopentadiene and methylcyclopentadiene were further studied to illustrate the applications of this array.

Miscellaneous

A preliminary investigation of a potential new chromatographic packing showed that tetrachloroterephthaloyl moieties could be most effectively bonded to silica surfaces through a two step reaction sequence. The initial step involved bonding aliphatic ester groups to the silica support surface through a trifunctional silicon atom. This was followed by a transesterification procedure.

Because ortho and para-hydrogen can be separated on alumina at liquid nitrogen temperatures and the rate of interconversion of these two species has been of interest over the years, we attempted the separation of these species and the interconversion on the new superconductors ($\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$). Our reasoning was that the magnetic properties of the superconductors at low temperatures might lead to enhanced separation of these species (since para hydrogen has unpaired spins and might be repelled). Despite the attraction of this idea and a number of experiments which were encouraging we were unsuccessful during the final period of this project. A number of experimental factors came to the fore which will have to be overcome to really test whether or not this approach will work. We hope to get back to this investigation.

Publications

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8. "Multicolumn Gas Chromatographic Reactor Studies of the Dissociation Reactions of Dicyclopentadiene and Its Methyl Derivatives", by T. D. Griffith, Alexander H. T. Chu and Stanley H. Langer, The Chemical Engineering Journal, 36, 73 (1987).

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